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Temperature modulated DSC studies of melting and recrystallization in polymers exhibiting multiple endotherms

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Abstract

Temperature-modulated DSC (TMDSC) is used to characterize melting and recrystallization in polymers exhibiting multiple melting endotherms. Poly(ethylene-2,6-naphthalenedicarboxylate)(PEN) and poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene)(PEEK) are chosen, and the data show the detailed contributions of thermal and processing histories to properties. The results are supplemented by standard DSC at different heating rates. By independent very rapid heating rate methods, the temperature at which the polymer first completely flows is used as a measure of the end of melting of crystals originally present in the sample, and is shown to be well below the final DSC melting point because of recrystallization during the DSC heating scan. This is true even for long annealing times at moderately high temperatures. The TMDSC signal detects endothermic peaks or shoulders corresponding to the melting of crystals originally present in the sample, and such information are not available from standard DSC because of offsetting exothermic and endothermic signals. The TMDSC data prove that the “low endotherm”—routinely detected by standard DSC a few degrees above isothermal annealing temperatures—is not a true “low endotherm”, but is a superposition of early melting of secondary crystals with almost simultaneous exothermic recrystallization. It is not a distinct endotherm because the degree of recrystallization measured in the non-reversing signal of TMDSC increases continuously up to and sometimes through the final melting region. This description of the thermal scan considers both primary crystals, secondary crystals, and recrystallization during the heating scan. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There is substantial interest in quantifying the nature of recrystallization and other thermal events related to metastability [1] of polymer crystals because of the importance of recrystallization on elevated temperature properties such as warp, dimensional stability, creep, softening, and heat deflection temperature. On the processing side there are also many issues which would benefit. For example, properties including high-temperature coalescence and adhesion of heated pellets and the additional heat generated via crystallization are crucial in the solid state polymerization processing of polyesters [2] including poly(ethylene-2,6-naphthalenedicarboxylate) (PEN).

Temperature-modulated DSC (TMDSC) is a relatively new technique [3–6] which subjects a sample to a linear heating ramp with a superimposed low frequency temperature oscillation (modulation) resulting in a modulation in the heating profile. TMDSC thermal analysis provides the “total” heat flow—such as that from conventional DSC—and the heat capacity-related (reversible) component of the heat flow. The difference between the reversing signal and the total is the non-reversing (NR) component [3–6]. The reversing signal is excellent for quantifying the glass transition (Table 1) and separates the glass transition completely from other non-reversing processes such as enthalpy relaxation and crystallization as is well known in the literature [3–6]. Exothermic events are completely absent from the reversing signal, helping in the resolution of the different thermal events. Unfortunately, both the reversing and non-reversing signals can contain components of endothermic crystal melting, and the relative fractions depend on the types of crystals present and the experimental conditions. Much of the complexity of analysis of TMDSC stems from the contribution of the crystal melting to both signals [3–6].

The physics of NR-melting has been summarized many years ago by Wunderlich, as have experimental techniques to measure such melting without reorganization effects, i.e. without a change in the metastability of the polymer system [1]. In recent experiments, Okazaki and Wunderlich show

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Table 1
TMDC (2°C/min) data after isothermal crystallization including glass transition temperatures, and heats of melting and crystallization (all temperatures in °C, ΔH in J g^{-1}, and ΔC_p in J g^{-1} K^{-1})

	ΔC_p	T_g	$\Delta H_{endo,low}$[a]	$\Delta H_{exo,NR}$	$\Delta H_{endo,NR}$	$\Delta H_{endo,R}$	ΔH_{total}	%X	$T_{m,true}$[b]
PEN									
170°C, 80 min	0.104	129	1.6	37.9	17.1	60.3	41.1	24.2[c]	245
210°C, 30 min	0.128	127	0[d]	21.0	15.1	54.6	48.7	28.7[c]	250
240°C, 18 hrs	0.084	128.5	–	–	54.4	15.7	70.1	41.2[c]	278
PEEK									
210°C	0.11	155	2.9	35.6	4	83.8	55	34.4[c]	329

[a] Obtained from total heat flow.
[b] $T_{m,true}$ is the melting point of the crystals “originally” present measured using the rapid heating rate technique described in the experimental.
[c] Percent crystallinities were calculated from heat of fusion for one hundred percent crystalline PEN given in Experimental, and 160 J/g for PEEK.
[d] At 10°C/min, the low endotherm is 3 J/g.

that in PET there is significant reversible melting because of “molecular nucleation” [5,6]. Molecular nucleation occurs when chains or chain segments melt near or on high-melting crystals, and then with negligible cooling, they can nucleate and recrystallize on these existing unmelted crystals. While this molecular nucleation process decreases due to annealing, it can occur continuously under “isothermal” conditions with an oscillation amplitude of 1°C and a frequency of one reciprocal minute, and contributes to the so-called reversible signal in quasi-isothermal measurements. The “complete” melting of lamellae will contribute to non-reversing melting as discussed in the next section.

A DSC heating scan on a typical polymer contains many non-equilibrium effects, including a large amount of reversible melting due to metastability of crystal morphologies in most polymers [1]. Although difficult, the interpretation of non-equilibrium DSC thermal trace is necessary to understand effects of thermal history on properties because some of the morphologies which dominate properties are erased during attempts at equilibrating the morphology. We feel that TMDSC provides additional information on the melting and crystallization portions of the thermal scans on such systems.

Years ago, several research efforts addressed the complexity of the DSC data for polymers such as PET [7–9] and poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) [10–16]. PEN is also relatively well studied by DSC [17–19] and X-ray [18,19], and the DSC data for PEEK have been correlated with various models of morphology development by X-ray techniques [13,20–24]. The DSC results for PET, PEEK and PEN show very similar patterns. Because of the subtle complexities in the DSC data, many models have been proposed for crystallization and melting of PET, PEN, PEEK, and related semicrystalline polymers. At present, no single model has a strong consensus [7–17].

The model of Zhou and Clough [9] for DSC of isothermally crystallized PET qualitatively incorporates both dual crystal populations, early melting and recrystallization. In this model, early melting of secondary crystals contributes to the low endotherm region, melting of primary crystals to the middle endotherm which is always present but not always distinguishable, and the final endotherm contains significant contributions from the recrystallized species formed during heating. The morphological development studied by temperature scanning small angle X-ray scattering (SAXS) [24,25] has been related [25] to the model of Zhou and Clough. As compared to the dual melting endotherm cases, the triple endotherm behavior observed by Zhou et al. [9] and others [1,25] actually makes it easier to separate and understand the three distinct processes which we believe to occur during the heating of PEN, PEEK, PET and related systems. Again, because of the standard DSC experiment is complex and sometimes misleading, one can actually show that for double melting one detects the typical low endotherm as expected, but the middle endotherm due to melting of “primary crystals” merges with the upper (recrystallization) endotherm [26], and especially in polymers like PEEK the middle endotherm is never clearly resolved or even detected as a shoulder in most cases by standard DSC [10,11,19]. This suggests that double melting is actually triple melting even though standard DSC cannot resolve the two highest transitions for a variety of reasons explored by TMDSC and another independent technique in this report.

1.1. Interpretation of TMDSC

The following summarizes contributions to the TMDSC data for many semi-crystalline polymers. Recall, we wish to describe methods for interpreting the thermal analysis experiment where the non-equilibrium structures obtained from polymer processing are deemed important, and would eventually desire to have the ability to obtain this information in experiments taking about the same time as standard DSC.

1. The non-reversing endothermic signal is typically due to complete melting of separate lamellae or stacks of lamellae [1,5]. In certain cases of perfected crystals with melting points not too far from their equilibrium melting point, the crystals cannot recrystallize fast enough because of a low degree of under cooling. This slow

recrystallization kinetics lead to high levels of non-reversing melting in a typical 2°C/min heating scan. Annealing polyesters at high temperatures (within ca. 20°C of final melting point) results in systems which have high T_m relative to their equilibrium melting point (example given later), and a very large non-reversing melting endotherm contribution.

2. The reversing endothermic signal is due to partial melting of lamellae. They are then able to rapidly recrystallize due to templating of the just melted chains as they recrystallize on existing crystals [5]. This recrystallization occurs even though there is no local “cooling” in the temperature-modulated profile because of the small modulation amplitude relative to the underlying heating rate. The physics of this process has been discussed in detail [5,6,27].
3. Crystallization exotherms only contribute to the non-reversing signal, making this a very powerful technique for separation of exotherms from glass transitions, reversible melting, or other heat capacity related events. Unfortunately, exothermic and endothermic non-reversible events can both occur simultaneously, nor can they be completely resolved from each other [27]. Since they can offset each other, one must be cautious when interpreting and comparing magnitudes. Recognition of this explains why standard DSC and TMDSC are difficult to interpret for many polymers [6,27], especially those which are prone to recrystallization during the measurement [14,28].

2. Experimental

2.1. Materials and preparation

PEEK 150G with a weight average molecular weight of about 30 000 was obtained from ICI Ltd. PEN with a weight average molecular weight of about 45 000 determined by viscosity, was obtained from Teijan Chemical Co. Crystallized samples were generated from both the melt and the glass states. Cold crystallization refers to heating the sample from the amorphous glass to the crystallization temperature, and melt crystallization refers to cooling from the melt to the annealing temperature. For cold crystallized samples generated from the glass state, films 0.3 mm thick between sheets of Kapton® polyimide were held in the melt. PEN films were held at 290°C for 2 min, and PEEK films at 380°C for 2 min followed by a rapid quench to room temperature by rapidly removing from the hot surface and sandwiching between two cold metal plates. The amorphous films were then heated to 170°C at ~500°C/min by dropping the film into a small temperature controlled brass chamber with N2 sweep. The temperature of the chamber and the heating rate were calibrated by imbedding thermocouples in the polymer films. The chamber consisted of heating coils in a large metal block with a cylindrical hole, where a 25 ml brass container was inserted. The lid was insulated and nitrogen was introduced with a needle. Temperature was controlled by placing a thermocouple at the bottom of the chamber.

The melt-crystallized samples were prepared by using 0.3 mm thick films and holding them in the melt at 290°C for 2 min. These samples were then immediately isothermally annealed using the small brass chamber. After annealing, all samples were quenched to room temperature at ~500°C/min.

2.2. Rapid heating rate technique

To measure the fusion of crystals “originally” present in the sample at heating rates fast enough to avoid recrystallization, a section of sample is quickly pressed against a temperature-controlled surface. This is equivalent to measuring melting points under zero entropy production [1] and is determined by inspection of viscoelastic properties (flow) and verified by immediately quenching and measuring crystallinity of the particle by DSC or density [29]. One expects that the following measurement, done properly, will measure the temperature at which the primary crystals are completely melted, i.e. the end of the melting range of originally present crystals without reorganization. Typically, the inspection of viscoelastic properties consists of quickly determining whether the complete flow of the entire sample occurs during the first fraction of a second, or in less obvious cases we examined the level of liquid transfer from the bottom of the sample to the metal surface. A metal block provides a controlled temperature surface, which is calibrated by covering a micro-thermocouple with a porous thermal insulator. As the surface temperature is varied, one polymer particle is used for each temperature to prevent elevated temperature recrystallization. A high degree of softening to a rubbery state was not considered to be complete melting for relatively low molecular weight polymers like PEEK and PEN, and this method was verified for low molecular weight semi-crystalline polymers where the liquification is easy to measure. For the lower temperature annealed samples, unpublished results for PET show that our determination of the end of melting for the original crystals present in the system is consistent with the end of the “initial distribution of crystal melting temperatures” predicted by Qiu et al. [26] from analysis of DSC data.

2.3. DSC

A TA Instruments (Newcastle, DE) 2920 DSC was used in these experiments, and the signal processing was provided by the manufacturer [30] and discussed in other work [31]. A standard heating ramp of 2°C/min was chosen and a modulation period of 60 s and a modulation temperature amplitude of 0.32°C was chosen based upon the recommended specifications [30], and our experience with semi-crystalline polymers. A N_2 purge was used for all experiments. Baseline calibration was performed regularly with empty pans at 2 and 10°C/min, and a four point

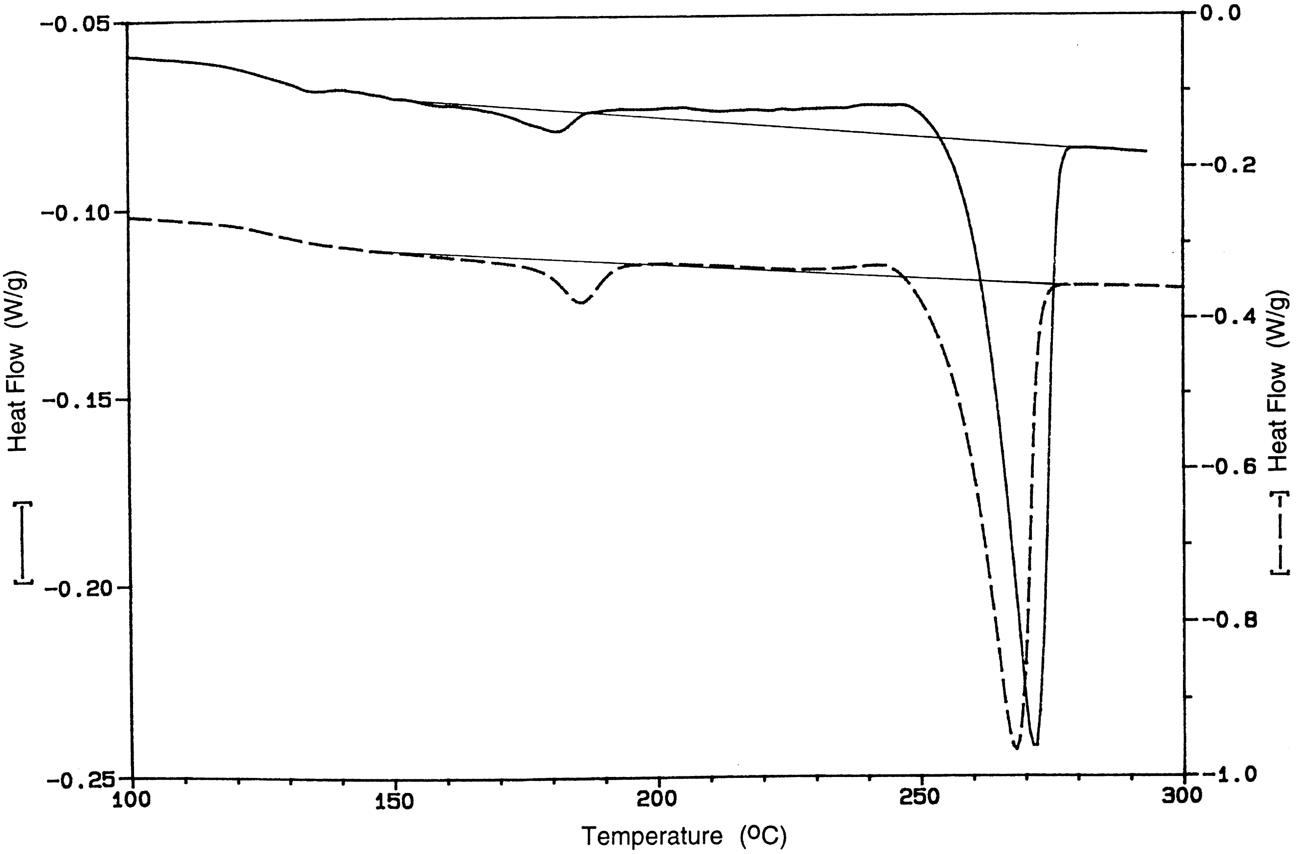

Fig. 1. Standard DSC (total) at heating rates of 2°C/min (solid curve) and 10°C/min (dashed). The PEN sample was cold-crystallized at 170°C for 80 min.

temperature calibration was performed with different metal standards. Careful baseline calibration is crucial for polymers exhibiting broad and weak transitions. The cell constant was calculated by standard analysis of an Indium standard, the heat capacity calibration constant for the modulation calibration was done using a standard sapphire sample [30]. To reduce heat flow lags, sample masses of 6–8 mg consisting of flat single layer polymer films were used. For each sample, three TMDSC experiments at 2°C/min were performed to test for reproducibility, and repeat runs on all samples were obtained at 10°C/min.

The modulation temperature amplitude is small relative to the underlying heating rate, and the modulated profile is heating only. At steady state, the residual heat flow detected in the zero heating rate section of the modulation cycle can be used as a measure of a non-reversing exothermic or endothermic process [27,31,32].

There is a large discrepancy in the literature for the heat of fusion of 100% crystalline PEN with values ranging from 103 J/g [17] to 190 J/g [18]. From density, DSC heat of fusion, and a measured crystal density of 1.407 g/ml, we obtained a preliminary value of heat of fusion of 100% crystalline PEN of 170 ± 10 J/g, which is used to calculate the fractional crystallinity in Table 1.

3. Results

Standard DSC data for 170°C, 80 min cold crystallized PEN at heating rates of 2 and 10°C show the expected trend [7,14,15,19] with the high temperature melting endotherm moving to higher temperatures at the lower heating rates (Fig. 1). The 10°C scan shows only a slight hint of an exotherm taking place above 175°C. Low temperature endotherms are observed at both temperature scan rates. The low endotherm is sharper and at a higher temperature in the 10°C/min scan. The small deviation of the heat flow from the baseline, especially in the 2°C/min data, provides a hint of a stronger, lower temperature exothermic contribution starting at ca. 180°C. This shift in the endotherm is due to the greater extent of recrystallization during the slower scan. For example, the exotherm will naturally shift to lower temperatures at lower heating rates [14]. Since such crystals will not superheat, the heating rate will not affect the onset significantly. Contrary to this, the extent of recrystallization at low temperatures will depend substantially on heating rate [14,26]. The data reinforce the complications of standard DSC and the modification of the morphology during the heating scan [14,15].

The NR–TMDSC data in Fig. 2 verify the suspected

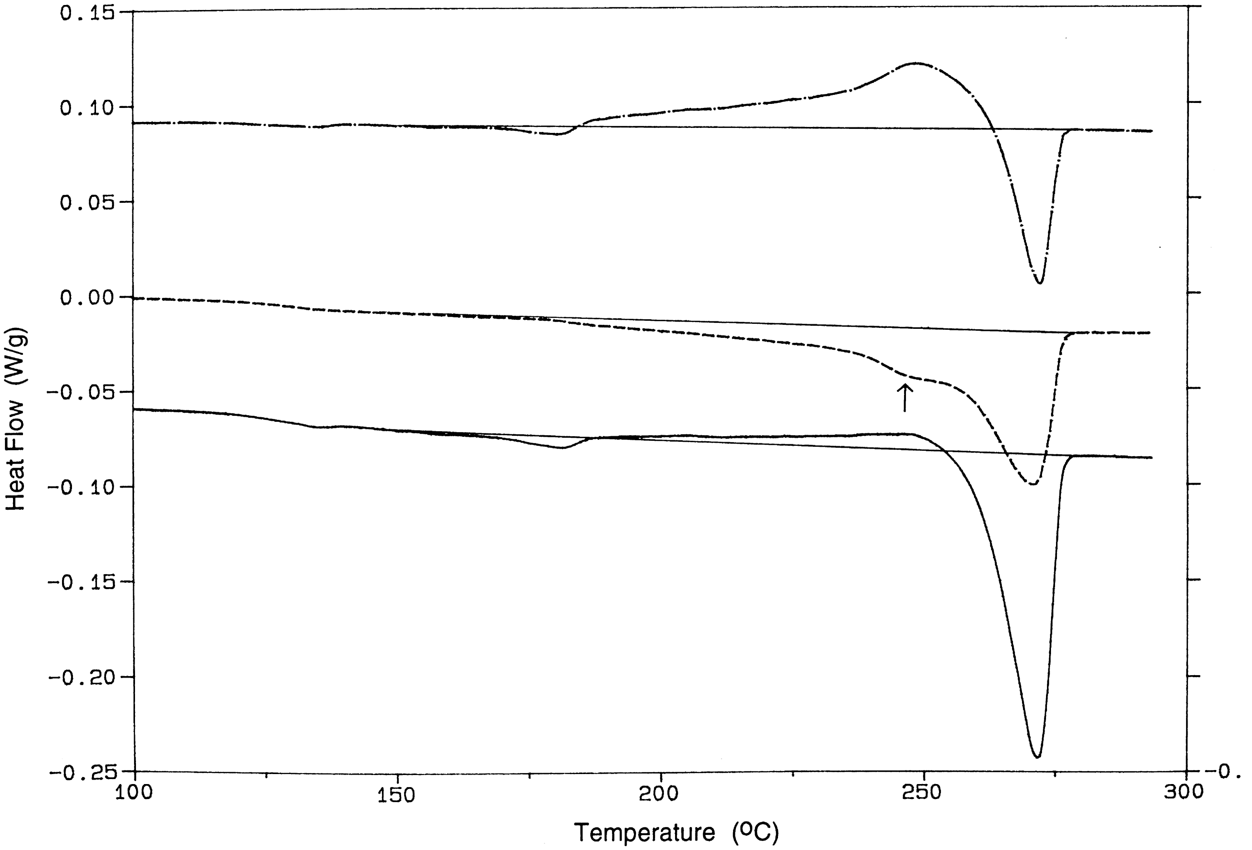

Fig. 2. Total (solid curve), reversing (dashed) and non-reversing (dot-dash) TMDSC data. All data are plotted on the same relative scale, and the total signal is the sum of the R and NR signals. The sample was annealed under the same conditions as in Fig. 1. The melting temperature of crystals "originally" present in the sample equals 245°C and was independently measured by the rapid heating rate technique discussed in the Experimental, and this temperature is indicated by the arrow on the plot (See text).

recrystallization where a strong exotherm is seen starting at ca. 180°C, just after the small endothermic dip. Just before the NR exotherm, the reversing melting endotherm starts at about 175°C, even though it is very weak at these lower temperatures. At ca. 245°C there is a broad shoulder in the reversible melting. The melting point of crystals "originally" present in this sample measured independently with the rapid heating rate technique is 245 ± 3°C (see Section 2) which corresponds to this shoulder region. This melting point should correspond to the end of melting of primary crystals, but it seems to occur in the middle of the shoulder region (Fig. 4) presumably because the recrystallization and melting of the recrystallized species are so dominant that the shoulder region is distorted. There is no hint of the melting of the "originally" present crystals in the standard DSC for this sample (Fig. 1), although for high heating rates the melting point of species initially present is approximately measured in some polymers [14,26]. Thus, TMDSC can detect this important quantity representative of the initial morphology, and once this is established other independent verification are less important. At slightly higher temperatures of about 250°C, the maximum in the NR exotherm is clearly seen, even though there is very little hint of this in standard DSC. This is indicative of massive reperfection which is typical of almost all annealing conditions except very high temperature ones. The NR endotherm in the final melting region occurs at a slightly higher temperature than the reversible endotherm, as is typical. The integrated thermal quantities are given in Table 1.

The variable heating rate data for the 210°C (30 min) melt crystallized PEN show similar trends to the 170°C annealed sample, where recrystallization shifts the final melting region to higher temperatures at the slowest heating rates (Fig. 3), and the kinetics of recrystallization at lower temperatures shift and change the magnitude of the exotherm contribution just above 210°C. The separated exotherm is seen more clearly in Fig. 4. A middle endotherm is detected at about 250°C (Fig. 3), and is representative of the true endotherm of the primary crystals formed during isothermal annealing at 210°C. It is smaller than one would expect because of the convoluted and compensating effects of NR melting and recrystallization in the region around 250°C. Fig. 4 shows the details of the melting and recrystallization, with explanations parallel

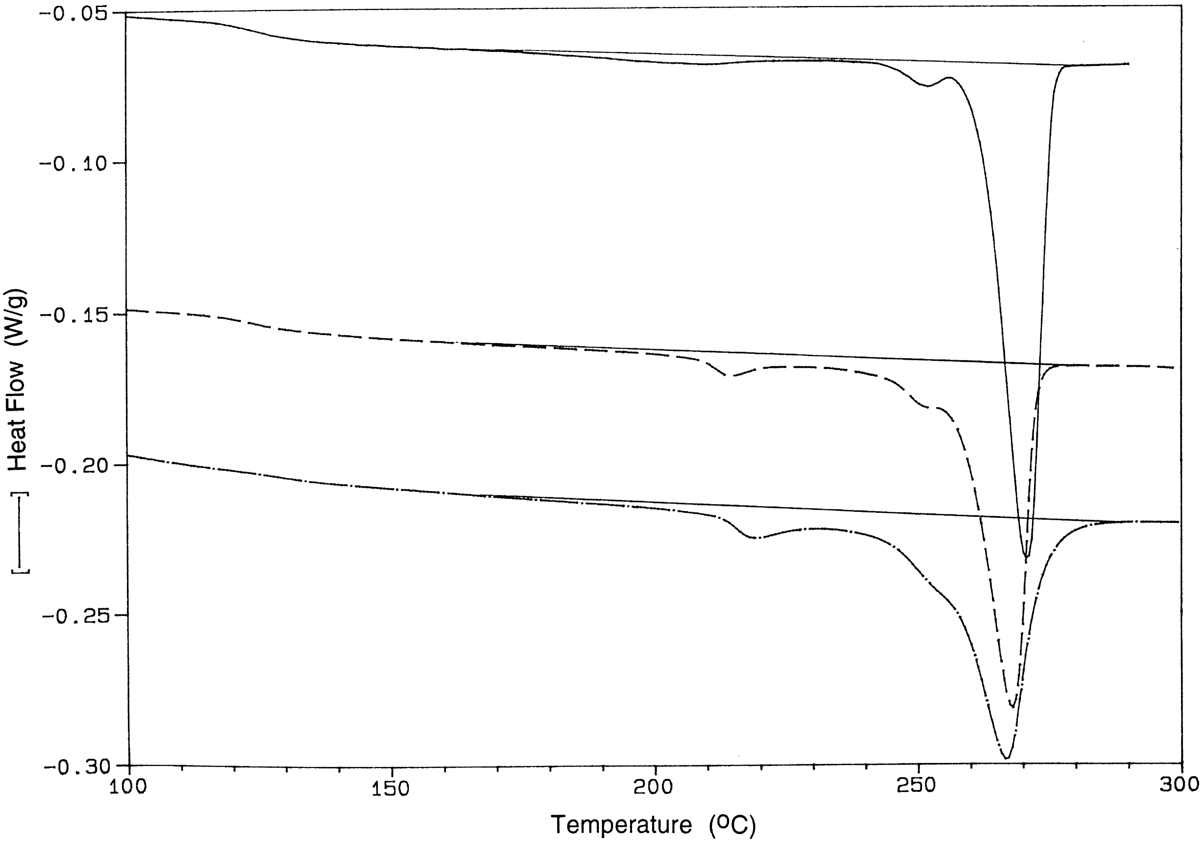

Fig. 3. Standard DSC (total) at heating rates of 2°C/min (solid curve), 10°C/min (dashed), and 40°C/min (dot-dash). The PEN sample was cold-crystallized at 210°C for 30 min.

with the discussion of the data in Fig. 2. The melting point of primary crystals of 255 ± 5°C obtained from the shoulder in the reversing data in Fig. 4 correlates well with the independently measured melting point of crystals originally present equal to 250 ± 3°C determined by the rapid heating rate technique.

PEEK is also well studied by DSC, including variable heating rate studies [14,15,19]. The results in Fig. 5 characterize the substantial exotherm which is not well characterized in standard DSC, and show the typical double endotherm behavior in the total signal [11–19]. The exotherm has been estimated for PEEK in previous studies [14] by variable heating rate DSC, in analogy to the previous model of Rim and Runt [28]. Because of the exotherm, a middle endotherm due to melting of primary crystals is not visible in the TMDSC data or especially in the total signal (Fig. 5). Notice that the independently measured (using rapid heating rate technique) melting points of crystals “originally” present indicated by the arrow on the plot is 329°C, and this approximately correlates with the NR exotherm and a very small shoulder on the reversing endotherm. In the Introduction we discussed the similarity of double and triple melting for isothermally crystallized samples, and such behavior shows why triple melting detected by DSC is rare in PEEK [19] even though it must be occurring.

4. Discussion

An interesting question is whether any thermal history in PEN, PET or related polymers will lead to a morphology which is stable to recrystallization during the DSC measurement, i.e. a zero entropy production melting process [1]. This topic has been reviewed in detail [1], but it is still useful to consider the new understanding derived from TMDSC. In PEN the annealing temperature must be surprisingly high. One example is given in Fig. 6 (top) for PEN annealed at 240°C for 18 h. The standard (total) signal shows a sharp melting point at 271°C, the non-reversing data show no hint of a recrystallization exotherm before the final melting region. The melting point of crystals originally present determined by the rapid heating rate technique is 278 ± 3°C, which agrees well with the end of melting determined by DSC which is 279°C. This proves that this is a thermal history which results in melting of species present in the original sample which are not affected significantly by the heating scan, and the evolution of such

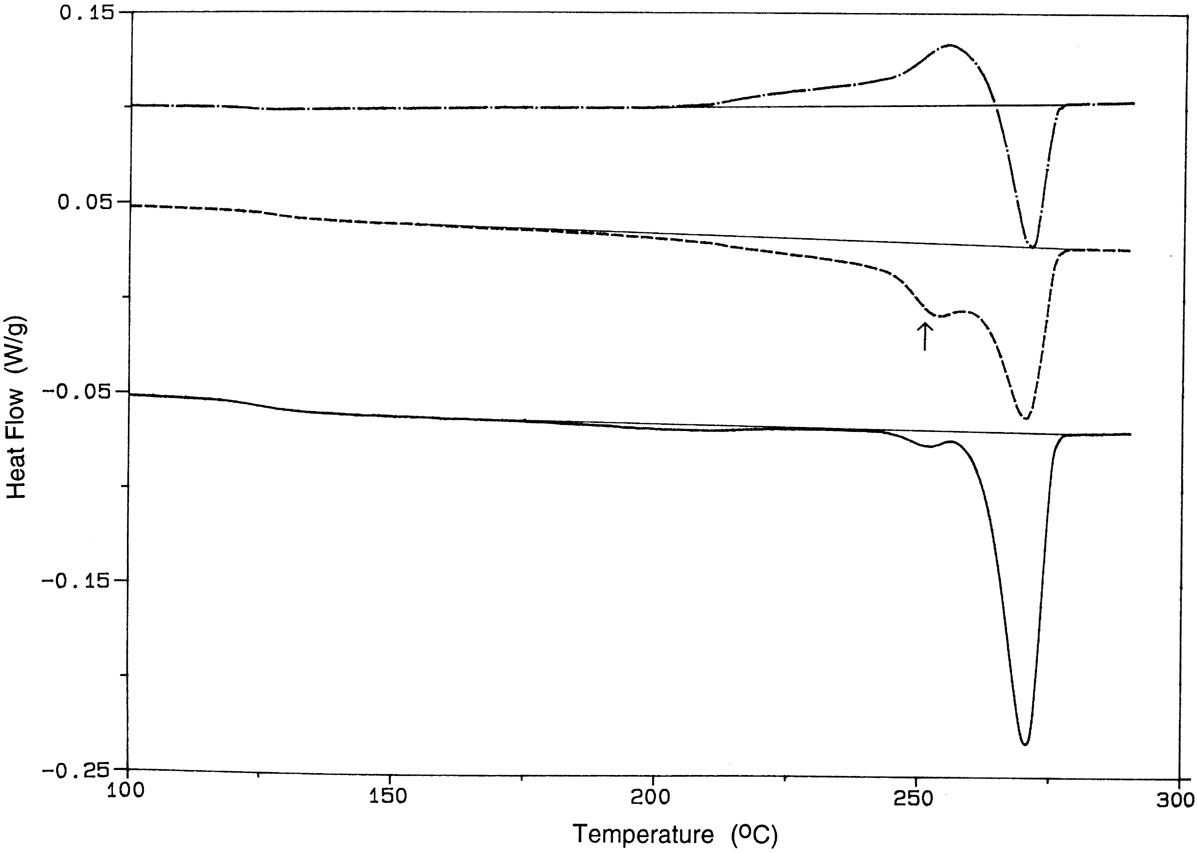

Fig. 4. Total (solid curve), reversing (dashed) and non-reversing (dot-dash) TMDSC data plotted on the same relative scale. The PEN sample was annealed under the same conditions as in Fig. 3. The melting temperature of crystals "originally" present equals 278°C and was independently measured by the rapid heating rate technique discussed in the experimental section, and this temperature is indicated by the arrow on the plot (see Section 2).

species with time and temperature and the correlation with changes in morphology would add to additional understanding [26]. The hint of a higher melting fraction in Fig. 6 is probably related to the very high melting fraction observed by Buchner et al. [18] after very high annealing at 270°C.

The data in Fig. 6 also verify the well-known phenomena [1] where at high enough annealing temperatures and long enough time, secondary crystals become equivalent to primary crystals [25], which is equivalent to the sharpening of the "initial distribution of crystal melting temperatures" quantified by Qiu et al. [26]. Here, both secondary and primary are relatively stable and will not recrystallize during the heating scan leading to one sharp, high temperature endotherm. The process leading to such a high single endotherm in PET has been studied in some detail recently by SAXS and TMDSC [25], and previously by a variety of techniques including DSC [1,26]. The evolution of the distribution of initial crystal melting points during high temperature annealing, and the melting point distribution of species which had recrystallized during the DSC scan has been theoretically examined [26]. In polyesters like PEN and PET, transesterification reactions [1,2,25] at high temperatures contribute to accelerated mobility and facilitate such "crystal perfection", or at least the shift to higher melting points. Thus, the trends at elevated temperatures may be different for other polymers such as PEEK where such interchange reactions contribute negligibly.

The TMDSC data in Figs. 2 and 4 show the unique contribution of the technique in characterizing the broad recrystallization exotherms which dramatically show how recrystallization dominates the results, even for a relatively "well crystallized" (210°C, 30 min) sample (Fig. 4). Because of offsetting exotherm and endothermic processes, the exotherm is barely detected by standard DSC or DSC at different heating rates, as was shown previously by Lee and Porter [14,15], and many others. Such data reinforce the idea that even long crystallization times at relatively high temperatures will result in a metastable system which will show signs of recrystallization during the heating scan, which can be readily studied by TMDSC. The TMDSC is not completely quantitative in characterization of the recrystallization exotherm, because of the possibility of non-reversing simultaneous endothermic activity which could reduce the apparent magnitude of the measured exotherm.

TMDSC data for very short isothermal crystallization times suggest that the low endotherm forms quite rapidly in these systems because substantial secondary crystal

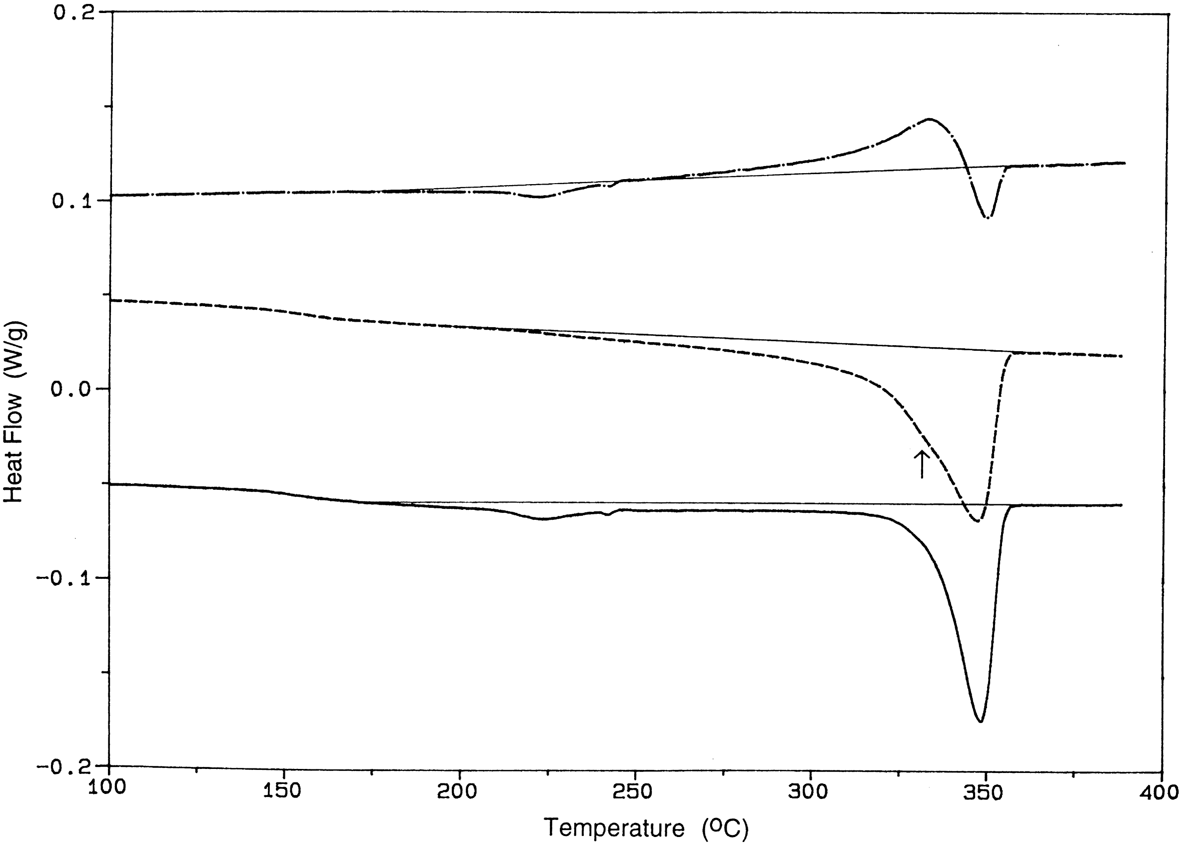

Fig. 5. Total (solid curve), reversing (dashed) and non-reversing (dot-dash) TMDSC data for PEEK annealed at 210°C for 66 h, plotted on the same relative scale. The melting temperature of crystals "originally" present equals 329°C and was independently measured by the rapid heating rate technique discussed in the experimental section, and this temperature is indicated by the arrow on the plot (see Section 2).

populations form during primary crystallization. Time resolved SAXS data confirm that large populations of secondary crystals form during the nominal "primary" crystallization regime [23,25]. Thus, low melting crystals are formed immediately and apparently can cause a low endothermic contribution. In many cases it is present but cannot be measured with standard DSC because the start of the low endotherm is washed out by the large exotherm evolved during DSC heating, normally for very incomplete initial crystallization. The TMDSC data in Figs. 2 and 4 also illustrate that the low endotherm is only a small part of the increasingly strong melting and recrystallization with increasing temperature. Since early melting has little time dependence, and recrystallization is strongly dependent on time, it is likely that almost any shape of the low endotherm can be obtained by changing the DSC heating rate [14,15]. Similar variations with heating rate have been modeled quantitatively in recent theoretical work [26]. Because of this, evaluation of the low endotherm by standard DSC in terms of its relationship to the kinetics and the development of secondary crystals is ill-advised.

For PEN annealed for 80 min at 170°C, careful examination indicates that secondary crystal melting is initially non-reversing over a very narrow temperature range where the endotherm first starts between 170 and 180°C. At temperatures around 180°C and above, recrystallization and melting also contribute to the reversing signal due to the large degree of melting and recrystallization. We can conclude that this non-reversing melting between 170 and 180°C in Fig. 2 is due to complete melting of entire defective lamellae or entire defective stacks, and it is a general trend that we have seen in TMDSC studies of several polymers. This non-reversing contribution might be expected if the secondary crystals are "separate" stacks of thin crystals [16,20] in the gaps between primary stacks which "completely" melt with no chance for molecular nucleation under the experimental time-scales [31]. The "separate" population or at least a broad distribution has been verified by SAXS [19,24,25] and other techniques [16]. Because reversing melting also contributes starting at about 180°C, just above the start of the non-reversing melting which is at 170°C, the overlap is enough to cause uncertainty in the interpretation. Other discussions of the low endotherm region in a different polymer include the suggestion of contributions due to enthalpy relaxation of interphase species [33].

In the Introduction the model of Zhou and Clough [9] was used to explain DSC triple melting, where melting of

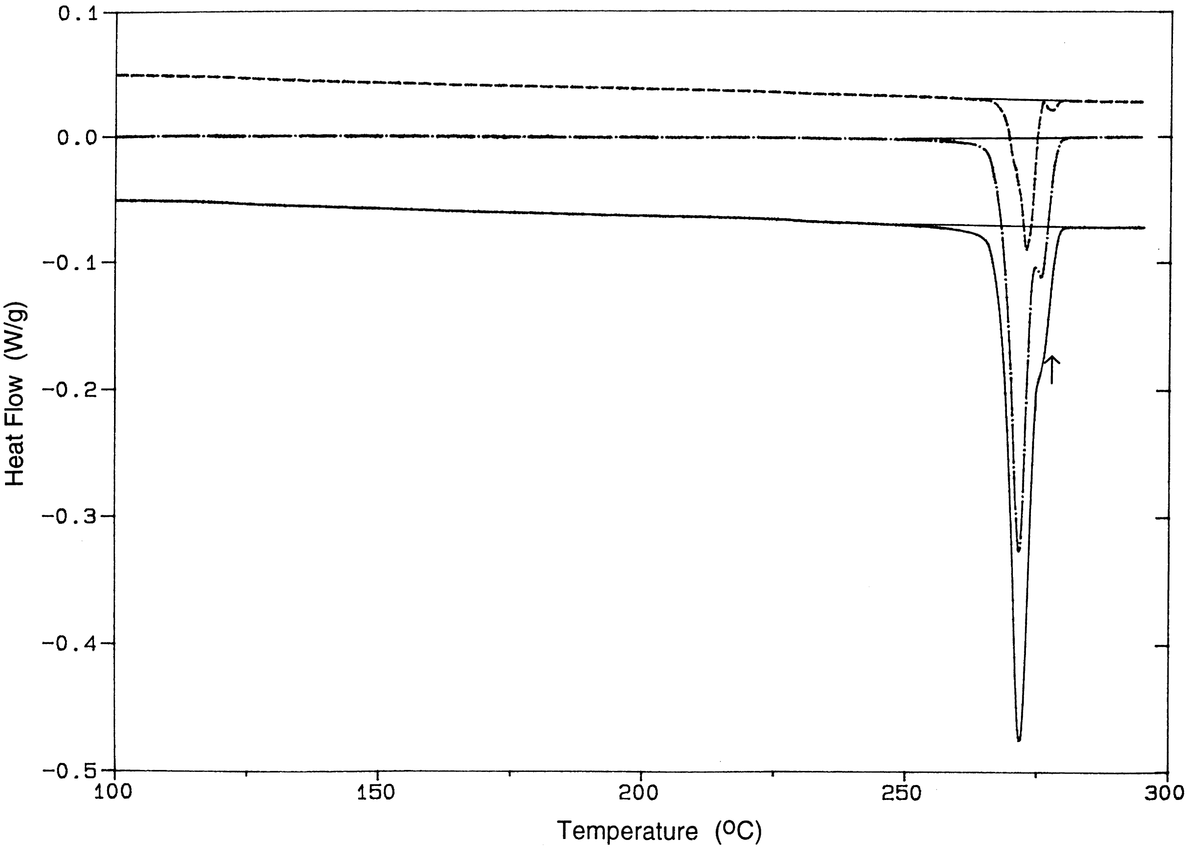

Fig. 6. Total (solid curve), reversing (dashed) and non-reversing (dot-dash) TMDSC data for PEN annealed at 240°C for 18 h, plotted on the same relative scale. The melting temperature of crystals "originally" present equals 278°C and was independently measured by the rapid heating rate technique, and this temperature is indicated by the arrow on the plot (see Section 4).

secondary crystals was followed by recrystallization which broadly overlaps with melting of primary crystals, with a final endotherm which was attributed to melting of the recrystallized species. TMDSC and independently measured melting points of the temperature of complete melting of the original crystals, determined by the rapid heating rate technique discussed in Section 2, verify this model. There are many similarities with the recent theory of Qiu et al. [26] which considers a "broad initial distribution of crystal melting temperatures" which effectively accounts for both secondary and primary crystal species. Experimentally, we can estimate the "initial distribution of crystal melting temperatures" by TMDSC, but unfortunately the technique is constrained to low heating rates. The high temperature limit of the end of melting of pre-existing primary crystals can actually be determined with high accuracy using our rapid heating rate technique measurement (see Table 1, Figs. 2–6). Standard DSC at high heating rates also allows one to estimate the initial distribution of primary crystals with some complications. The initial distribution was assumed to be broad but continuous in the theoretical treatment [26], but the reversing TMDSC data (Fig. 4) suggests that the low endotherm due to the melting region of secondary crystals is somewhat distinct from the middle endotherm attributed to primary crystal melting. The TMDSC data are incomplete because of overlapping thermal events, and a more detailed study will be completed in the future. TMDSC does quantitatively explain the DSC traces of systems demonstrating multiple melting endotherms, and contributes to resolving much of the controversy in interpretation of standard DSC over the past few decades.

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